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Syntheses and Absorption Spectra of New Azo Dyes Containing an Azulene Ring

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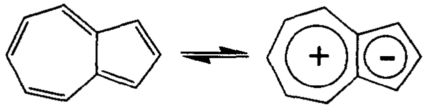
ABSTRACT

*New azo dyes containing an azulene ring were prepared by the diazo coupling reaction of ethyl 2-hydroxyazulene-3-carboxylate derivatives with aromatic amines. An unusual azo–hydrazone tautomerism was observed for the ethyl 1-(4'-*N,N*-dimethylaminophenylazo)-2-hydroxyazulene-3-carboxylate derivatives containing a strong electron-donating group (such as* N,N*-dimethylamino) in the diazo component amine, as shown by electronic spectra data measured in polar and nonpolar solvents. It was concluded that a 2-hydroxyazulene ring has a greater tendency to exist in the keto-form than the 2-hydroxynaphthalene ring, which has a similar 10 π electron system.*

1 INTRODUCTION

The stability of the azulene system has often been rationalized in terms of resonance structures, such as in Scheme 1, in which the five-membered ring acquires a cyclopentadienyl carbanic character while the seven-



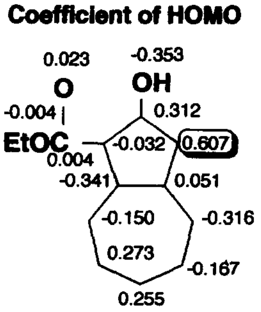
Scheme 1.

membered ring loses an electron to become tropylium ionic in nature.[1,2] On the other hand, a naphthalene ring, which is also a 10 π electron system, does not have a polarized structure. Ethyl-2-hydroxyazulene-3-carboxylate derivatives (**2a** and **2b**) were prepared and new azo dyes containing the azulene ring were derived from them to study the influence on the absorption spectra of the polarized structure in comparison with dyes from methyl-2-hydroxy-3-naphthoate. Furthermore, relationships between absorption spectra and substituents in the diazonium components were examined.

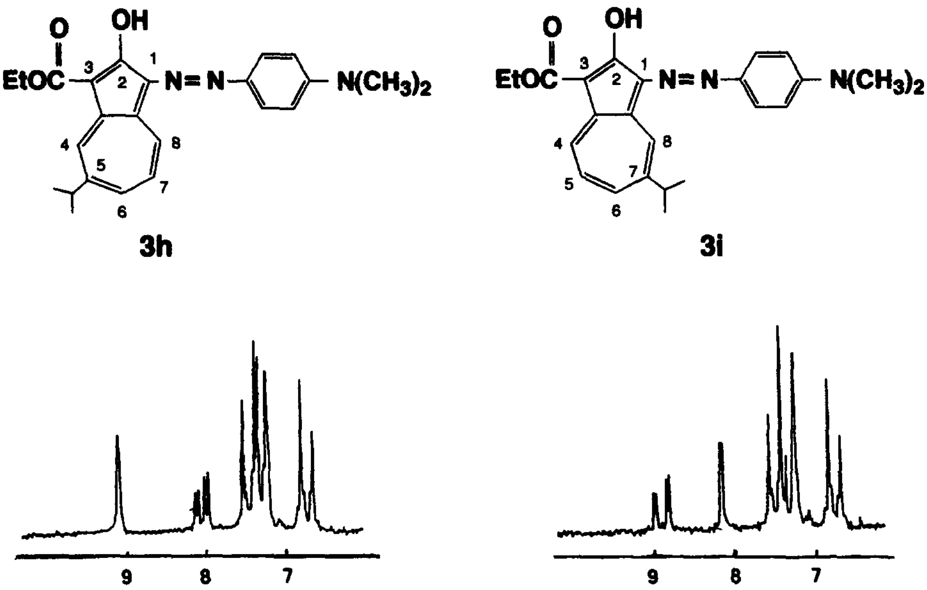
2 RESULTS AND DISCUSSION

2.1 Diazo coupling reaction of 2 with several aromatic amines

It has been established that electrophilic substitution of azulenes occurs at the 1- and 3-positions, which coincide with the positions calculated to have the highest electron density on theoretical consideration.[3] Although diethyl 2-hydroxyazulene-1,3-dicarboxylate (**1a**) substituted by an electron-withdrawing group at the 1- and 3-positions could be attacked by electrophiles at the 6- and/or 3-positions,[4] ethyl 2-hydroxyazulene-3-carboxylate (**2a**), which was prepared by decarboethoxylation of **1a** according to literature procedures,[5] reacted with diazonium components at only the 3-position, at which the HOMO coefficient is highest, as shown in Scheme 2.



Scheme 2.



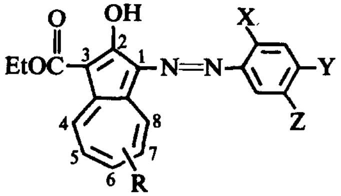
Scheme 3. NMR spectra in aromatic area of dyes **3h** and **3i**.

The coupler **2b** was also prepared by the above method from **1b** (5-isopropyl derivatives of **1a**). In this case, a mixture of 5- and 7-isomers was obtained and the ratio of isomers was estimated to be about 1 : 1 from integral strengths at the 1-position in the ^{1}H-NMR spectra. This isomer mixture was used in the diazo coupling reaction, because of the difficulty in isolating individual isomers by conventional methods. The diazo coupling reaction of **2b** with 4-dimethylaminobenzene diazonium salt resulted in the formation of both isomers, and these were separated by column chromatography and purified by repeated recrystallization. Their structures were confirmed by ^{1}H-NMR spectra as shown in Scheme 3. For dye **3h**, the broad peak of the proton at the 4-position was observed at lower field than the double doublet peaks at the 8-position due to the influence of the carbonyl group of the adjacent ethyl ester group. The reverse spectrum pattern was observed for dye **3i**. Detailed structural analyses of the isomers will be reported separately. The yield and melting points of the products are summarized in Table 1.

2.2 Absorption spectra of azo dyes

Electronic absorption spectra of the azoazulene dyes are summarized in Table 2. The absorption maxima shift to longer wavelength as the electron-donating ability of the substituent *Y* increases. PPP MO calculations indicated that the origin of these absorption bands was intramolecular

TABLE 1
Diazo Coupling Reactions of Azulene Derivatives with Several Aromatic Diazonium Salts



3

No.	*R*	*X*	*Y*	*Z*	*Yield (%)*	*m.p. (°C)*
3a	H	H	NO_2	H	77·4	249–251
3b	H	H	CN	H	60·1	221–223
3c	H	H	H	H	81·0	158–160
3d	H	H	CH_3	H	23·4	151–153
3e	H	H	OCH_3	H	38·5	153–154
3f	H	H	$N(CH_3)_2$	H	11·5	168–170
3g	H	OCH_3	[a]	OCH_3	12·0	273–274
3h	5-iso-Pro	H	$N(CH_3)_2$	H	40·0[b]	130–132
3i	7-iso-Pro	H	$N(CH_3)_2$	H	40·0[b]	179–180

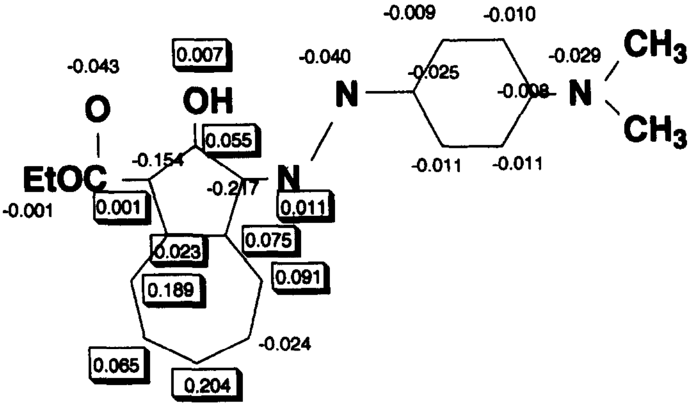
[a] N = N  $N(CH_3)_2$.

[b] Calculated from the NMR spectrum of mixture.

TABLE 2
Absorption Spectra of Dyes **3**

No.	λ_{max} ($\varepsilon \times 10^{-4}$)(*Benzene*)
3a	408(5·6), 473(1·7)
3b	405(4·1), 470(1·9)
3c	405(3·5), 495(1·5)
3d	407(4·6), 505(1·6)
3e	410(3·4), 524(1·5)
3f	425(2·1), 525(1·9), 615(1·6)
3g	417(2·3), 638(3·8), 705^{sh}(2·2)
3h	427(3·7), 534^{sh}(3·1), 569(3·1), 607^{sh}(3·0)
3i	423(3·6), 532^{sh}(3·2), 568(3·2), 605^{sh}(3·1)

sh: shoulder.



Scheme 4. Differences of electron densities between ground and excited state.

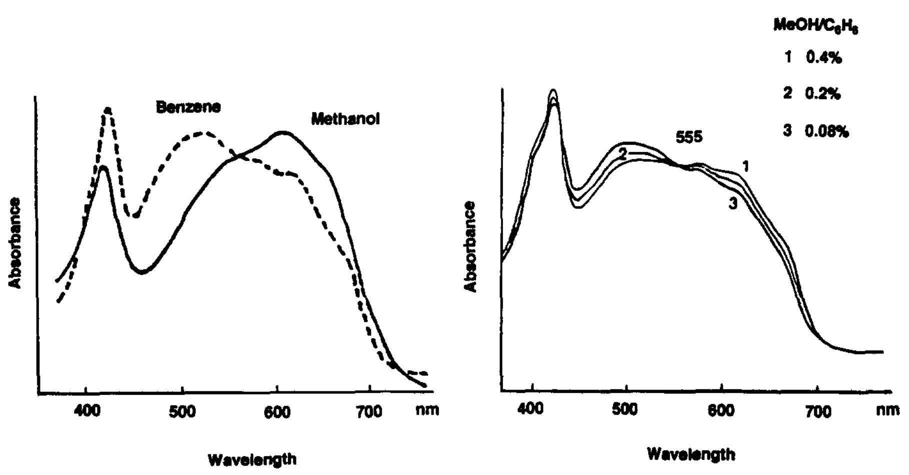
charge-transfer from the diazo component to the azulene ring (Scheme 4). Therefore, the spectra were affected by substituents. Only dyes **3f**, **3h** and **3i** showed a significant change of absorption extinction in polar and nonpolar solvents, and two peaks were observed; the absorption extinction was stronger in the shorter wavelength region in nonpolar solvents such as benzene, but in the longer wavelength absorption in polar solvents such as methanol (Table 3, Fig. 1(a)). An isosbestic point was observed at 555 nm for **3f**, depending on slight changes in the ratio of solvent (benzene and methanol) as shown Fig. 1(b).

In the case of a stronger electron-donating substituent than the *N*,*N*-dimethylamino group, for example as in dye **3g**, the absorption extinction at the longer wavelength was strong and the tautomerism shown by the change of solvent was no longer observed. On the other hand, dyes **3a**–**3e** did not show any significant change of λ_{max} in several solvents. Furthermore, the azo dye **4b** containing a naphthalene ring and which has similar structure to dye **3f** did not show any solvent effects

TABLE 3
Solvent Effect of Dyes **3f**, **3h** and **3i**

No.	λ_{max} ($\varepsilon \times 10^{-4}$)(*Benzene*)	λ_{max} ($\varepsilon \times 10^{-4}$)(*Methanol*)
3f	425(2·1), 525(1·9), 615^{sh}(1·6)	420(1·6), 550^{sh}(1·8), 610(2·0)
3h	427(3·7), 534^{sh}(3·1), 569(3·1), 607^{sh}(3·0)	423(3·4), 555^{sh}(3·6), 604(4·6)
3i	423(3·6), 532^{sh}(3·2), 568(3·2), 605^{sh}(3·1)	423(3·3), 550^{sh}(3·5), 608(4·6)

sh: shoulder.



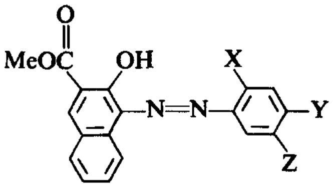
(a) (b)

Fig. 1. The change of absorption spectra between benzene and methanol.

(Table 4). It must be noted, however, that the small absorption of **4b** at longer wavelength region results from the contribution of the hydrazone-form.[6]

It is concluded that the azulene ring results in a greater tendency to azo–hydrazone tautomerism than the naphthalene ring (Fig. 2), especially when the substituent *Y* is a *N*,*N*-dimethylamino group; this is due to the azulene ring having a polarized structure.

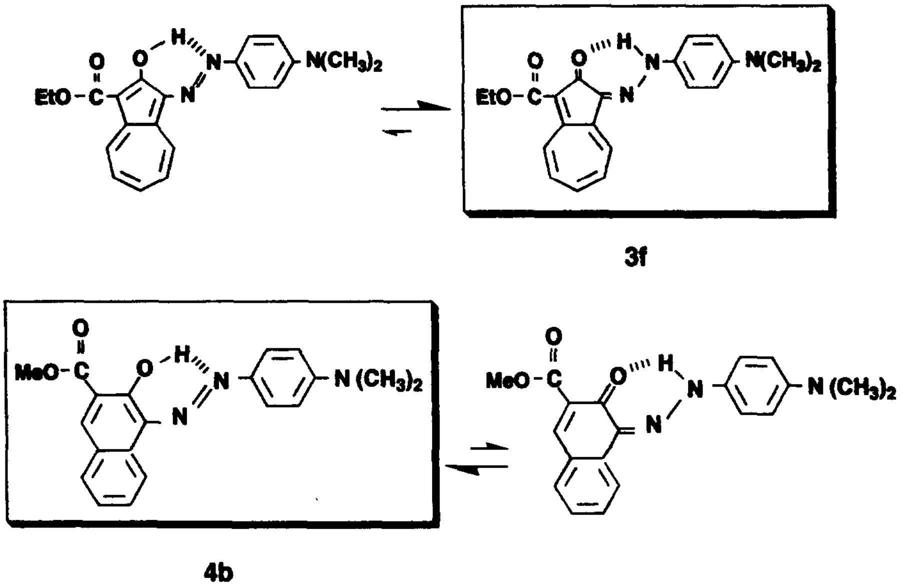
TABLE 4
Absorption Spectra of Dyes 4



4

No.	*X*	*Y*	*Z*	λ_{max} ($\varepsilon \times 10^{-4}$)(*Benzene*)	λ_{max} ($\varepsilon \times 10^{-4}$)(*Methanol*)
4a	H	H	H	489(1·5), 516(1·4)	490(1·8), 513(1·8)
4b	H	N(CH$_3$)$_2$	H	488(3·7), 507(3·3), 605^{sh}(0·4)	507(3·3), 605^{sh}(0·8)
4c	OCH$_3$	[a]	OCH$_3$	427(1·8), 607(5·5)	428(1·8), 608(4·6)

[a] N = N  N(CH$_3$)$_2$.
sh: shoulder.



3f

4b

Fig. 2. Azo–hydrazone tautomerism of **3f** and **4b**.

3 EXPERIMENTAL

All melting points were uncorrected. Visible spectra were recorded on a Hitachi EPS-3T spectrophotometer. ^{1}H-NMR spectra were recorded on a Nihon Denshi JNM-FX6OQ NMR spectrometer, unless otherwise stated in $CDCl_3$ solution, with tetramethylsilane as internal standard. Mass spectra were recorded on a Nihon Denshi JMS-DX303 spectrometer operating at 80 eV. Elemental analyses were recorded on a Yanaco CHN recorded MT-2. Column chromatography was carried out on silica gel (Wakogel C-300) using chloroform as eluent.

3.1 Materials

The diethyl 2-hydroxyazulene-1,3-dicarboxylate derivatives (**1a** and **1b**) and ethyl 2-hydroxyazulene-1-carboxylate derivatives (**2a** and **2b**) were prepared by the previously described method.^{5} Compound **2a** was purified by column chromatography followed by recrystallization from ethanol; compound **2b** was the mixture of the 5-isopropyl and 7-isopropyl azulene derivatives and was liquid at room temperature. Aromatic amines were of commercial grade and were used without further purification. 4-(4'-*N*,*N*-Dimethylaminophenylazo)-2,5-dimethoxyaniline was prepared by the diazo coupling reaction of 4-*N*,*N*-dimethylaminobenzene diazonium salt with 2,5-dimethoxyaniline.

3.2 Diazo coupling reaction of 2a and 2b with aromatic amines: general procedure

Compound **2a** (red needles) (1·57 g, 7 mmol) was added to ethanol (20 ml) and 28% sodium ethylate (1·7 g, 7 mmol), with vigorous stirring, and water (800 ml) was added in order to obtain a solution. A solution of 4-*N*,*N*-dimethylaminobenzene diazonium chloride (prepared by diazotizing 4-*N*,*N*-dimethylaminoaniline (0·95 g, 7 mmol), dissolved in concentrated hydrochloric acid (1·2 ml, 14 mmol) and water (5 ml), with sodium nitrite (0·53 g, 7·7 mmol) in 5 ml of water) was added, with constant stirring to the above solution. The product was filtered, washed with water, dried, column-chromatographed with benzene and finally recrystallized from ethanol to give the black–blue dye **3f**.

3.3 Characterization and identification of products

Compounds **1a** and **2a** were known compounds and were characterized by data described in the literature[5] and by the following.

1a: m.p. 144–145°C; ^{1}H-NMR: 1·49(t, 6H, CH_3), 4·52(q, 4H, CH_2), 7·56–7·84(m, 3H, aromatic), 9·21–9·50(m, 2H, aromatic), 11·76(b, 1H, OH).

1b: m.p. 104–105°C; ^{1}H-NMR: 1·41(d, 6H, CH_3), 1·51(t, 6H, CH_3), 3·21(1H, CH), 4·51(q, 4H, CH_2), 7·65(d, 2H, aromatic), 9·33(t, 1H, aromatic), 9·45(b, 1H, aromatic), 11·75(b, 1H, OH).

TABLE 5
Elementary Analyses Data of Dyes 3

No.	*Molecular formula*	*Analysis (%)*					
		C		*H*		*N*	
		Calc.	*Found*	*Calc.*	*Found*	*Calc.*	*Found*
3a	$C_{19}H_{15}N_3O_5$	62·46	62·45	4·14	3·96	11·50	11·60
3b	$C_{20}H_{15}N_3O_3$	69·56	69·05	4·38	4·10	12·17	12·14
3c	$C_{19}H_{16}N_2O_3$	71·24	71·08	5·03	4·89	8·74	8·89
3d	$C_{20}H_{18}N_2O_3$	71·84	71·38	5·39	5·41	8·38	8·48
3e	$C_{20}H_{18}N_2O_4$	68·56	68·65	5·15	5·57	8·00	7·66
3f	$C_{21}H_{21}N_3O_3$	69·41	69·52	5·79	5·84	11·57	11·81
3g	$C_{29}H_{29}N_5O_5$	66·02	65·48	5·50	5·95	13·27	12·25
3h	$C_{24}H_{27}N_3O_3$	71·11	71·24	6·67	6·99	10·37	10·23
3i	$C_{24}H_{27}N_3O_3$	71·11	69·89	6·67	6·53	10·37	10·10

TABLE 6
Characterization Data of Dyes **3**

No.	*m/e*	*^{1}H-NMR*
3a	365	1·45(t, 3H, *j* = 7 Hz), 4·44(q, 2H, *j* = 7 Hz), 7·26–7·61(m, 3H), 7·53(d, 2H, *j* = 9 Hz), 7·58–7·92(m, 1H), 8·30(d, 2H, *j* = 9 Hz), 8·73–9·03(m, 1H)
3b	345	1·45(t, 3H, *j* = 7 Hz), 4·44(q, 2H, *j* = 7 Hz), 7·19–7·63(m, 7H), 7·91–8·15 (m, 1H), 8·81–9·03(m, 1H)
3c	320	1·46(t, 3H, *j* = 7 Hz), 4·46(q, 2H, *j* = 7 Hz), 7·16–7·62(m, 8H), 8·04–8·24 (m, 1H), 8·94–9·16(m, 1H)
3d	334	1·46(t, 3H, *j* = 7 Hz), 2·37(s, 3H), 4·45(q, 2H, *j* = 7 Hz), 7·11–7·62(m, 7H), 8·00–8·13(m, 1H), 8·87–9·08(m, 1H)
3e	350	1·46(t, 3H, *j* = 7 Hz), 3·84(s, 3H), 4·45(q, 2H, *j* = 7 Hz), 6·94(d, 2H, *j* = 9 Hz), 7·29–7·58(m, 3H), 7·50(d, 2H, *j* = 9 Hz), 8·08–8·23(m, 1H), 8·94–9·13(m, 1H)
3f	363	1·47(t, 3H, *j* = 7 Hz), 3·04(s, 6H), 4·46(q, 2H, *j* = 7 Hz), 6·83(d, 2H, *j* = 9 Hz), 7·20–7·64(m, 3H), 7·51(d, 2H, *j* = 9 Hz), 8·15–8·33(m, 1H), 9·02–9·24(m, 1H)
3g	527	1·46(t, 3H, *j* = 7 Hz), 3·10(s, 6H), 4·02(s, 3H), 4·12(s, 3H), 4·46(q, 2H, *j* = 7 Hz), 6·80(d, 2H, *j* = 9 Hz), 7·40(s, 1H), 7·58(s, 1H), 7·91(d, 2H, *j* = 9 Hz), 7·25–8·15(m, 4H), 8·83–9·02(m, 1H)
3h	405	1·35(d, 6H, *j* = 7 Hz), 1·47(t, 3H, *j* = 7 Hz), 3·01(s, 6H), 2·77–3·25(1H), 4·46(q, 2H, *j* = 7 Hz), 6·74(d, 2H, *j* = 9 Hz), 7·20–7·55(2H), 7·47(d, 2H, *j* = 9 Hz), 8·11(dd, 1H, *j* = 9 Hz, *j* = 3 Hz), 9·13(b, 1H)
3i	405	1·37(d, 1H, *j* = 7 Hz), 1·46(t, 3H, *j* = 7 Hz), 3·02(s, 6H), 2·86–3·18(1H), 4·45(q, 2H, *j* = 7 Hz), 6·77(d, 2H, *j* = 9 Hz), 7·18–7·40(2H), 7·50(d, 2H, *j* = 9 Hz), 8·17(d, 1H, *j* = 2 Hz), 8·95(dd, 1H, *j* = 10 Hz, *j* = 2 Hz)

2a: m.p. 75–76°C; ^{1}H-NMR: 1·51(t, 3H, CH$_3$), 4·53(q, 2H, CH$_2$), 6·75(s, 1H, H of five-membered ring), 7·33–7·58(m, 3H, aromatic), 8·04–8·23(m, 1H, aromatic), 8·83–9·02(m, 1H, aromatic), 10·8(b, 1H, OH).

2b: liquid; ^{1}H-NMR: 6·56 and 6·60(s, 1H, H of five-membered ring); mass: 258; 4-(4'-*N*,*N*-dimethylaminophenylazo)-2,5-dimethoxyaniline: m.p. 162–163·5°C; ^{1}H-NMR: 2·17(s, 6H, N(CH$_3$)$_2$), 3·95(b, 6H, OCH$_3$).

Relevant data for dyes **3** and **4** are given in Tables 5, 6 and 7.

TABLE 7
Characterization Data of Dyes **4**

No.	*m.p. (°C)*	*m/e*	*^{1}H-NMR*
4a	180–181	306	3·99(s, 3H), 7·30–7·91(m, 8H), 8·40–8·56(2H)
4b	176–179	349	3·09(s, 6H), 4·01(s, 3H), 6·80(d, 2H, *j* = 9 Hz), 7·37–7·88 (m, 3H), 7·81(d, 2H, *j* = 9 Hz), 8·42(s, 1H), 8·86(d, 1H, *j* = 8 Hz)
4c	273–274	513	3·11(s, 6H), 3·99(s, 3H), 4·06(s, 3H), 6·80(d, 2H, *j* = 9 Hz), 7·30–8·00(m, 7H), 8·40–8·59(2H)

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